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<b>(21) International Application Number:</b> PCT/EP93/02560 <b>(22) International Filing Date:</b> 21 September 1993 (21.09.93)  <b>(30) Priority data:</b> 9219962.9 22 September 1992 (22.09.92) GB  <b>(71) Applicant (for all designated States except US):</b> EXXON CHEMICAL PATENTS INC. [US/US]; 1900 East Linden Avenue, Linden, NJ 07036 (US).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only) :</b> CAPROTTI, Rinaldo [IT/GB]; White Witch House, East Hanney, Oxfordshire OX12 0HQ (GB). SMITH, Anthony, Kitson [GB/GB]; 18 Western Avenue, Woodley, Reading, Berkshire RG5 3BH (GB).		<b>(74) Agents:</b> MANSELL, Keith, Rodney et al.; Exxon Chemi- cal Limited, Exxon Chemical Technology Centre, P.O. Box 1, Abingdon, Oxfordshire OX13 6BB (GB).  <b>(81) Designated States:</b> AU, BG, BR, CA, CZ, FI, HU, JP, KR, NO, PL, RO, RU, SK, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> ADDITIVES FOR ORGANIC LIQUIDS  <b>(57) Abstract</b>  Certain known and novel additives have proved effective in suppressing or inhibiting the foaming tendencies of organic li- quids, particularly petroleum fuels.		

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## Additives for Organic Liquids

This invention concerns additives useful as suppressors or inhibitors of the foaming tendencies of organic liquids.

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The foaming tendency of an organic liquid can be a major constraint to industrial usefulness. Foaming may render a liquid unsuitable as a solvent or diluent for chemical processes involving agitation. Foaming can further interfere with the pumping efficiency of such liquids, and the resulting foam may obscure the dials of flow gauges, making accurate measures of volume difficult.

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The problem of foaming is particularly important in the distribution of organic liquids such as liquid petroleum products, especially fuels and lubricants. Such liquids typically pass through a distribution network, involving pumping through pipelines, or a series of storage tanks. In such distribution systems, foaming can substantially increase the pumping times of large quantities of liquid. In addition, severe foaming can lead to the overflow of excessive foam from tanks during filling, resulting in wastage and the hazard of spilt liquid.

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The problem of foaming of organic liquids has been addressed by the use of additives which impart a reduced foaming tendency to the liquids in question. Such additives are known in the art, examples being organo-silicon copolymers, or derivatives of such polymers. Examples of these are the siloxane-polyoxyalkylene block copolymers described in United States Patent No 20 3,233,986, which consist of one or more siloxane blocks attached to one or more oxyalkylene blocks, a major proportion of which is composed of oxyethylene and/or oxypropylene groups. Such organo-silicon polymers have proved effective in reducing the foaming tendencies of a variety of organic liquids. Other classes of organo-silicon polymers, including fluorinated derivatives are also known, and have been used for their foam-reducing properties.

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However, in certain organic liquids, the use of such organo-silicon materials as additives to suppress or inhibit foaming has created problems. In particular, their application to organic liquids subject to subsequent combustion leads to the concomitant combustion of the organo-silicon polymer, resulting in the production of silicon oxides such as silicon dioxide. Silicon oxides generated by combustion take the form of finely-divided solid matter, and thus contribute to the

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quantity of particulate matter emitted from the combustion zone. This contribution to the emitted particulate matter is of particular concern in applications under legislative pressure to reduce emission levels, especially particulate emissions. In particular, the combustion of petroleum products, especially of fuels and lubricants, is under increasing legislative scrutiny.

In addition, particles of silicon oxides may, by poisoning the catalyst surface, interfere with the action of catalyst systems employed to reduce the emissions of particulate and other products of incomplete combustion. The effectiveness of particulate traps, which function by filtering out particulate matter may also be reduced, the silicon oxide particles plugging the fine pores through which exhaust gases pass.

Thus there exists a need for materials, useful as suppressors or inhibitors of the foaming tendencies of organic liquids, which do not give rise to silicon oxides upon combustion. Further, there exists a need for said materials to be capable of combustion to gaseous products, such that their contribution to the quantity of particulate matter generated by combustion will be negligible.

It has now surprisingly been found that certain ashless additives, being obtainable by the reaction between

- (a) a polyamine possessing at least one primary or secondary amino group, and
- (b) a carboxylic acylating agent

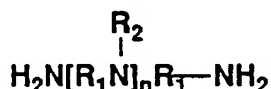
are effective in suppressing or inhibiting the foaming tendencies of organic liquids.

Compositions corresponding to the above reaction products have been described in the art. Such compositions include the automotive fuel dispersants described in UK Patent No 1,124,611 being the products of reaction between a polyalkylene polyamine and a hydrocarbyl-substituted succinic acid (or functional derivative thereof), having as a substituent a substantially aliphatic hydrocarbon group containing 30-200 carbon atoms. The hydrocarbyl substituent is preferably derived from a C<sub>2</sub>-C<sub>5</sub> olefin polymer. UK 1,124,611

further describes the constitution of the reaction product as complex, being a likely mixture of amide, diamide and imide products. Hydrocarbyl-substituted succinamide and succinimide fuel dispersants are further described in numerous references, for example EP-A-147,240.

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EP-A-240,255 describes anti-fouling agents suitable for use in gasoline fuels, said agents having the formula



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wherein  $\text{R}_1$  is  $\text{C}_2\text{-C}_4$ .

$\text{R}_2$  is hydrogen or  $\text{R}_3-\overset{\text{O}}{\parallel}{\text{C}}$ ,  
 $\text{R}_3$  is hydrogen, alkyl, aryl, alkaryl or aralkyl; and  
 $n$  is an integer of 1 to 5.

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These anti-fouling agents are described to be particularly effective in controlling deposit build-up in fuel injection systems.

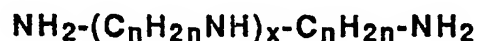
US Patent No 3,772,359 describes polyamides of a polyalkylene polyamine and an iso-fatty acid or mixture of an iso-fatty acid and a straight-chain fatty acid. The polyamides are further reacted with a mixture of an aldehyde and an alkyl hydroxy aromatic compound to form a product useful as a lubricant additive. For such polyamides to form a suitable starting material for this further reaction, they require at least one free basic nitrogen atom, i.e. a nitrogen possessing a

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replaceable hydrogen atom.

US Patent No 4,394,135 describes products of reaction between phenylstearic acid or isostearic acid and a polyamine of the formula

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wherein  $n$  is from 2 to 4 and  $x$  is 1 to 9. The polyamine reactant is employed in an amount sufficient to give a product in which every basic nitrogen atom has been acylated. Such reaction products are further said to impart improved

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detergency to liquid hydrocarbon fuels.

FR-A-1,584,938 describes amides containing at least one unreacted amino group, obtained by the reaction of di, tri and polyamines with higher carboxylic acids. Such products are useful during the refining of petroleum fractions, aiding the separation of water present initially as residual water haze.

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US Patent No 3,502,713 describes surface active compounds having low foaming tendencies, being the reaction products of an aromatic carboxylic acid with a dibasic acid and a diacylatable material. Such compounds are described as effective in a variety of aqueous systems.

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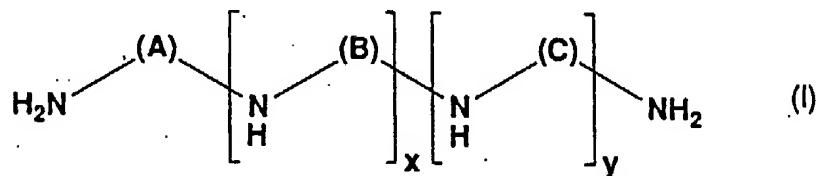
US Patent No 3,259,586 describes derivatives of N-substituted polyalkylene polyamines, useful as foam inhibitors in a variety of media, including mineral oil. The N-substituted nature of the polyamine is said to impart unusual properties to its derivatives, which include acylates. However, such polyamines are derived from unsubstituted polyalkylene polyamines via a multi-step reaction pathway, placing economic constraints on their industrial application. There exists a continuing need for compositions which inhibit foams in organic media and are more cost effective to produce industrially.

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20 In a first aspect, this invention provides the use, for suppression or inhibition of the foaming tendencies of an organic liquid, of a product obtainable by the reaction between

(a) a polyamine of the formula (I)

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wherein A, B and C are the same or different and each represents a hydrocarbyl group, and x and y are integers whose sum is in the range from 0 to 10, and

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(b) a carboxylic acylating agent

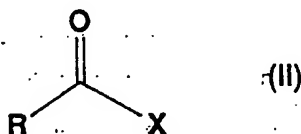
provided that, when the sum of x and y is 0 and (b) is selected from the group consisting of stearoyl, palmitoyl, myristoyl, lauroyl and oleoyl acylating agents, A does not represent ethylene or trimethylene.

- 5 In a second aspect, the invention provides a liquid composition comprising a major proportion of an organic liquid, and a minor proportion of an additive comprising a fully-acylated product of reaction between

(a) a polyamine of the formula (I) as hereinbefore described, and

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(b) a monocarboxylic acylating agent of the formula (II)



- 15 wherein R represents a hydrocarbyl group, and wherein X is a leaving group, provided that (b) is not phenylstearic acid, isostearic acid or tall-oil fatty acid,

- provided that, when the sum of x and y is 0 and R is selected from the group consisting of n-heptadecyl, n-hexadecyl, n-tetradecyl, n-dodecyl and cis-9-heptadecenyl, A does not represent ethylene or trimethylene.

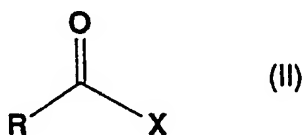
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In a third aspect, the invention provides a fully-acylated product of reaction between

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(a) a polyamine of the formula (I) wherein A, B and C are as hereinbefore described and x and y are integers whose sum is in the range of 1 to 10, and

- 30 (b) a monocarboxylic acylating agent of the formula (II)



wherein R represents a hydrocarbyl group, and wherein X is a leaving group, provided that (b) is not phenylstearic acid, isostearic acid or tall-oil fatty acid.

5 In a fourth aspect, the invention provides a process by which the foaming tendency of an organic liquid is suppressed or inhibited, comprising the addition of a product obtainable by the reaction between

(a) a polyamine of the formula (I) as hereinbefore described, and

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(b) a carboxylic acylating agent

provided that, when the sum of x and y is 0, A does not represent ethylene or trimethylene when (b) is selected from the group consisting of stearoyl, palmitoyl, 15 myristoyl, lauroyl and oleoyl acylating agents.

#### First Aspect of the Invention

In accordance with the first aspect of this invention, polyamines useful as 20 reactant (a) include those having the general formula (I).

In a preferred embodiment of the first aspect, the sum of x and y is in the range from 1 to 10. More advantageously, the sum of x and y is not more than 8, preferably not more than 6, more preferably not more than 4 and most preferably 25 not more than 2.

As used in this specification the term "hydrocarbyl" refers to a group having a carbon atom directly attached to the rest of the molecule and having a hydrocarbon or predominantly hydrocarbon character. Among these, there may 30 be mentioned hydrocarbon groups, including aliphatic (e.g. alkyl or alkenyl), alicyclic (e.g. cycloalkyl or cycloalkenyl), aromatic, aliphatic and alicyclic-substituted aromatic, and aromatic-substituted aliphatic and alicyclic groups. Aliphatic groups are advantageously saturated. Unsubstituted hydrocarbyl groups are preferred; however, if desired such groups may carry further 35 hydrocarbyl groups as substituents. Such groups may also contain non-hydrocarbon substituents provided their presence does not alter the predominantly hydrocarbon character of the group, examples including keto,



halo, hydroxy, nitro, cyano, alkoxy and hydroxyalkyl. If the hydrocarbyl group is substituted, a single (mono) substituent is preferred. Examples of substituted hydrocarbyl groups include 2-hydroxyethyl, 3-hydroxypropyl, 4-hydroxybutyl, 2-ketopropyl, ethoxyethyl, and propoxypropyl. The groups may also or  
5 alternatively contain atoms other than carbon in a chain or ring otherwise composed of carbon atoms. Suitable hetero atoms include, for example, nitrogen, sulfur, and, preferably oxygen. Advantageously, each hydrocarbyl group contains at most 10, preferably at most 8, more preferably at most 6 and most preferably at most 4, carbon atoms.

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In a more preferred embodiment of the first aspect, the polyamine reactant is an alkylene diamine or polyalkylene polyamine of the above formula where A, B and C are each alkylene groups containing up to 10, preferably at most 8, more preferably at most 6 and most preferably at most 4 carbon atoms. Thus the  
15 polyamine reactants preferred in the present invention include simple diamines for example ethylene diamine, propylene diamine, butylene diamine and pentylene diamine; polyalkylene polyamines for example diethylene triamine, triethylene diamine, tetraethylene pentamine, pentaethylene hexamine, di(methylethylene)triamine, dibutylene triamine, tributylene tetramine and  
20 dipentylene hexamine.

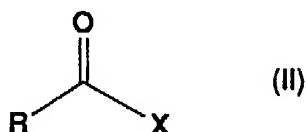
The alkylene groups constituting A, B and C may optionally be substituted by one or more hydrocarbyl groups as hereinbefore described. In a more highly preferred embodiment A, B and C are alkylene groups containing 1 to 3 carbon  
25 atoms, optionally substituted by one or more alkyl, alkenyl, alkoxy or hydroxyalkyl groups with hydroxyalkyl groups being most preferred. Most highly preferred embodiments of the polyamines suitable as reactant (a) include ethylene diamine and diethylene triamine.

30 The polyamine reactant may comprise a mixture of polyamines, each component being a polyamine having the aforesaid general formula (I). Of such mixtures, those comprising alkylene diamines and polyalkylene polyamines are preferred, such amines being optionally substituted by one or more hydrocarbyl groups. More preferred are mixtures comprising alkylene diamines and  
35 polyalkylene polyamines wherein said alkylene groups contain 1-3 carbon atoms, optionally substituted by one or more alkyl, alkenyl, alkoxy or

hydroxyalkyl groups. Most highly-preferred mixtures of polyamines include mixtures of ethylene diamine and diethylene triamine.

The carboxylic acylating agents useful as reactant (b) according to the first aspect contain one or more carboxylic acylating groups and a hydrocarbyl group sufficient to impart hydrocarbon solubility to the molecule. Suitable carboxylic acylating groups include carboxylic acid groups and derivatives thereof possessing a leaving group, i.e. a group capable of being displaced during reaction. Examples of such carboxylic derivatives include esters, anhydrides and acyl halides including acyl chlorides, acyl bromides and acyl iodides, although other carboxylic derivatives known in the art as acylating agents may be used to equal effect.

More preferred carboxylic acylating agents are monocarboxylic acylating agents of the formula (II):



where R represents a hydrocarbyl group, and where X represents a leaving group. Such preferred agents include fatty acid compositions, such as naturally-occurring fatty acids and derivatives of same. Preferably, such fatty acids or derivatives contain from 8 to 40, more preferably 10 to 30, even more preferably 12 to 24, and most preferably 12 to 18 carbon atoms. In such fatty acid compositions, R is preferably straight or branched-chain alkyl or alkenyl, and more preferably straight chain alkyl. Most preferred fatty acids include those selected from the group comprising lauric, myristic, palmitic, stearic, oleic and elaidic acids, stearic and oleic acids being most preferred.

The preferred fatty acid compositions useful in this invention may also comprise mixtures of fatty acids, having average carbon number within the preferred ranges hereinbefore described. Such specifically-preferred mixtures include mixtures of the above fatty acids, and naturally-originating mixtures such as coco-fatty acid fraction and cekanoic acid (a mixture of iso-C<sub>13</sub> fatty acids). Mixtures of naturally-originating fatty acids with the other fatty acids described above are also preferred.

The products according to the first aspect of this invention may be of mixed composition, where the polyamine selected as (a) contains more than one primary or secondary amino group. Thus, the product may comprise a mixture of simple amides, di- and higher poly-amides; imides and/or amidine reaction products where the nature of reactants (a) and (b) and the ratio in which they are combined permits such reactions to take place. Their definition in terms of reaction products thus describes most conveniently the range of possible compositions obtained in accordance with the use of this invention.

Reaction conditions suitable for generating the above reaction products are for example known in the art for promoting the acylation of polyamines. Thus, the reaction may be carried out by mixing the reactants (a) and (b), optionally in the presence of a mutual co-solvent, and heating the mixture sufficiently to cause reaction to occur, without raising the temperature above the decomposition temperature of the reactants or product. Alternatively, reactant (a) may be heated to reaction temperature and reactant (b) added over an extended period. Suitable temperatures are typically between 100° and 300°C, the exact temperature being determined by the nature of the selected reactants.

Examples of the preparation of products according to the use of this invention are found in US 4,394,135, and EP 147,240, to which further attention is directed.

The degree of acylation of polyamine (a) is generally dictated by the number of primary and/or secondary nitrogens present within the polyamine, i.e. the number of possible acylation sites, the proportions in which reactants (a) and (b) are mixed, and the time allowed for reaction. In accordance with the use of the invention, the product may be formed by the reaction of one mole of polyamine with at least one mole of the carboxylic acylating agent. Preferably, the product is formed by the reaction of the polyamine with at least two moles of the carboxylic acylating agent. More preferably, the product is formed by the complete acylation of the polyamine by the carboxylic acylating agent. Within this specification, the term 'full' acylation is used to define reactions where every amino group on the polyamine has undergone a condensation reaction upon addition of acylating agent (b). Thus, under 'full' acylation, each

polyamine amino group will react to evolve one equivalent of water, irrespective of the exact nature of the condensation reaction which occurs with the acylating agent (b).

5 Second Aspect of the Invention

In accordance with the second aspect of the invention, and in a more preferred embodiment of the first, the product may be formed by the full acylation of one mole of a polyamine of the formula (I) by a monocarboxylic acylating agent of the  
10 formula (II), provided that the acylating agent is not phenylstearic acid, isostearic acid, or tall-oil fatty acid.

Third Aspect of the Invention

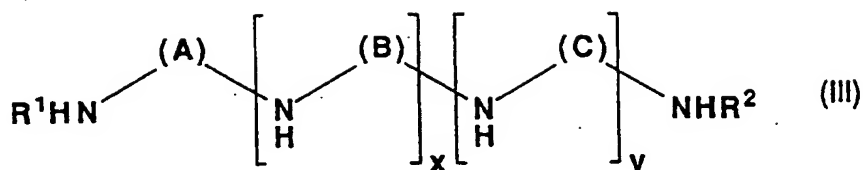
15 In accordance with the third aspect of the invention, and in more highly preferred embodiments of the first and second aspects, the product may be formed by the full acylation of one mole of a polyamine of the formula (I) provided that the sum of x and y is in the range from 1 to 10, by a monocarboxylic acylating agent of the formula (II), provided that the acylating agent is not phenylstearic acid,  
20 isostearic acid, or tall-oil fatty acid.

In both the second and third aspects of the invention, particularly suitable polyamines and monocarboxylic acylating agents are those preferred  
25 embodiments of the respective general formulae (I) and (II), described in accordance with the first aspect, subject to the conditions mentioned above.

In the fourth aspect of the invention, suitable and preferred polyamines and monocarboxylic acylating agents are those described in relation to the first  
30 aspect.

Fifth, Sixth and Seventh Aspects of the Invention

A further class of additives in accordance with this invention are those obtainable by the reaction of the carboxylic acylating agent (b) with one or more  
35 polyamines (a) of the general formula (III)



wherein A, B and C are as defined under the first four aspects of the invention,  
and wherein R<sup>1</sup> and R<sup>2</sup> maybe the same or different and each represents  
5 hydrogen or a hydrocarbyl group, provided that both R<sup>1</sup> and R<sup>2</sup> are not  
hydrogen, and x and y are integers whose sum is in the range from 0 to 10.

In a fifth aspect therefore, this invention provides a fully-acylated product of  
reaction between (a) a polyamine of the formula (III), and (b) a monocarboxylic  
10 acylating agent of the formula (II) previously defined under the first aspect of this  
invention.

In a sixth aspect, the invention provides a liquid composition comprising a major  
proportion of an organic liquid, and a minor proportion of an additive comprising  
15 the product of the fifth aspect.

In a seventh aspect, the invention provides the use, for suppression or inhibition  
of the foaming tendencies of an organic liquid, of the product of the fifth aspect.

20 In preferred embodiments of the fifth, sixth and seventh aspects, the polyamine  
reactant is a terminal N-substituted or terminal N,N'-disubstituted polyamine of  
the formula (III) where A, B and C are each alkylene groups containing up to 10,  
preferably at most 8, more preferably at most 6 and most preferably at most 4,  
carbon atoms. Thus these polyamine reactants include terminal N-substituted or  
25 terminal N,N'-disubstituted derivatives of simple diamines such as ethylene  
diamine, propylene diamine, butylene diamine and pentylene diamine, and  
terminal N-substituted or terminal N,N'-disubstituted derivatives of polyalkylene  
polyamines such as diethylene triamine, triethylene diamine, tetraethylene  
pentamine, pentaethylene hexamine, di(methylethylene)triamine, dibutylene  
30 triamine, tributylene tetramine and dipentylene hexamine.

In a more highly preferred embodiment of the fifth, sixth and seventh aspects of the invention,  $R^1$  and  $R^2$  of the polyamine reactant each independently represent hydrogen or an aliphatic hydrocarbyl group.

- 5 This aliphatic hydrocarbyl group is preferably a straight or branched chain alkyl, oxyalkyl or hydroxyalkyl group. Most preferably, it is a hydroxyalkyl group, for example a 2-hydroxyethyl group.

- Particularly preferred amines according to the fifth, sixth and seventh aspects  
10 are those in which one of  $R^1$  and  $R^2$  is hydrogen. Also advantageously, the sum of  $x$  and  $y$  in the polyamine is not more than 8, preferably not more than 6, more preferably not more than 4 and most preferably not more than 2.

- The polyamine reactant may comprise a mixture of polyamines, each  
15 component being a polyamine having the aforesaid general formula. Of such mixtures, those comprising terminal N-substituted or terminal N,N'-disubstituted alkylene diamines, and terminal N-substituted or terminal N,N'-disubstituted polyalkylene polyamines are preferred, such amines being optionally substituted by one or more hydrocarbyl groups. More preferred are mixtures  
20 comprising alkylene diamines and polyalkylene polyamines wherein said alkylene groups contain 1-3 carbon atoms, optionally substituted by one or more alkyl, alkenyl, alkoxy or hydroxyalkyl groups.

- The polyamine reactant may also comprise a mixture of polyamines of the  
25 formula (I) in combination with a mixture of polyamines of the formula (III).

- The organic liquids of the first, second, fourth, sixth and seventh aspects of the invention include a variety of hydrocarbon liquids, such as linear, non-linear and cyclo-aliphatic hydrocarbon solvents for example n-hexane, heptane, octane,  
30 n-decane, cyclohexane, as well as mixtures of such solvents with aromatic hydrocarbons. Particularly suitable are hydrocarbon solvents which are admixed to materials which increase the tendency of said solvents to foam.

- Especially suitable organic liquids are liquid hydrocarbon fuels, for example  
35 petroleum-derived fuels such as gasoline, kerosene, or distillate fuel oil. Of such fuels, distillate fuel oils, especially middle distillate fuel oils, are preferred.

Such middle distillate fuel oils generally boil within the range of from 110 °C to 500 °C, e.g. 150 °C to 400 °C. The fuel oil may comprise atmospheric distillate or vacuum distillate, or cracked gas oil or a blend in any proportion of straight run and thermally and/or catalytically cracked distillates. The most common middle  
5 distillate fuels are jet fuels, diesel fuels, heating oils and heavy fuel oils. The heating oil may be straight atmospheric distillate, or it may contain minor amounts, e.g. up to 35 wt%, or vacuum gas oil or cracked gas oils or of both.

Vegetable-based fuel oils are also suitable, for example rape seed oil or ester  
10 derivatives of rape seed oil, especially rape seed oil methyl and ethyl esters. Such vegetable-based fuels are preferably used alone or blended with petroleum-derived fuel oils. Similarly, blends of oxygenates such as alcohols, diols and/or ethers with petroleum-derived fuel oils may be advantageously used.

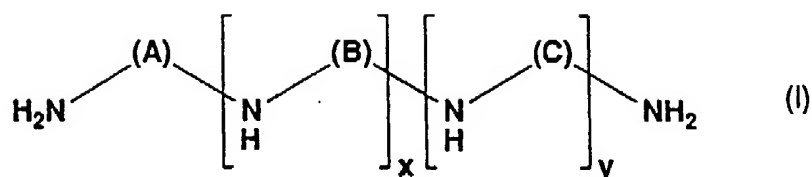
15 The liquid hydrocarbon fuels preferred in accordance with the first, second, fourth, sixth and seventh aspects of the invention may further contain any of the additives customarily present in such liquids, or known from the literature. For example, where the fuel is a gasoline fuel, it may contain anti-knock additives  
20 such as tetraethyl lead or cyclopentadienyl-manganese tricarbonyl compounds, or derivatives. Further, the gasoline may contain one or more dispersant or detergent additives, for example the hydrocarbyl-substituted amines well-known in the art. Other additives commonly present include plasticiser esters, for example adipates and mixtures thereof, scavengers, anti-oxidants, ignition  
25 improvers, metal deactivators, metallic salts useful as valve recession inhibitors, for example sodium salts of alkyl benzene sulphonic acids, and oxygenates such as alcohols and ethers.

Where the fuel is a middle distillate fuel oil, the fuel may contain one or more low  
30 temperature flow-improving additives known in the art.

In a eighth aspect therefore, this invention claims the use, for suppression or inhibition of the foaming tendencies of an organic liquid of an additive comprising both a product obtainable by the reaction between

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(a) a polyamine of the formula (I)



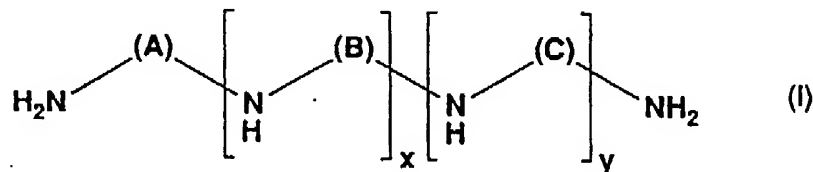
wherein A, B and C are the same or different and each represents a hydrocarbyl group, and x and y are integers whose sum is in the range from 0 to 10, and

(b) a carboxylic acylating agent,

and one or more low temperature flow improving additives.

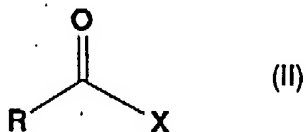
In a ninth aspect, this invention claims a liquid composition comprising a major proportion of an organic liquid and a minor proportion of an additive comprising both a fully acylated product of reaction between

(a) a polyamine of the formula (I)



wherein A, B and C are the same or different and each represents a hydrocarbyl group, and x and y are integers whose sum is in the range from 0 to 10, and

(b) a monocarboxylic acylating agent of the formula (II)



wherein R represents a hydrocarbyl group, and X represents a leaving group, provided that (b) is not phenylstearic acid, isostearic acid or tall-oil fatty acid,



and one or more low temperature flow improving additives.

Preferred under the eighth and ninth aspects are those products of reaction wherein reactant (a) is selected from those polyamines preferred under the first  
5 three aspects of the invention. Also preferred are those organic liquids preferred under the first, second, sixth and seventh aspects.

The one or more aforementioned low temperature flow improving additives may be selected from the group comprising:

10

(i) a comb polymer,

(ii) a polyoxyalkylene ester, ether, ester/ether or a mixture thereof,

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(iii) an ethylene/unsaturated ester copolymer,

(iv) a polar, organic, nitrogen-containing wax crystal growth inhibitor,

(v) a hydrocarbon polymer,

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(vi) sulphur carboxy compounds, and

(vii) hydrocarbylated aromatics.

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Such low temperature flow improvers will now be discussed in more detail.

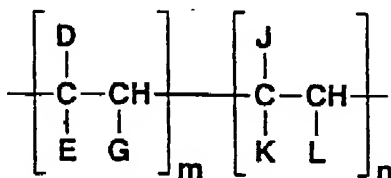
(i) **Comb Polymers**

Comb polymers are polymers in which hydrocarbyl groups are pendant from a  
30 polymer backbone and are discussed in "Comb-Like Polymers. Structure and Properties", N. A. Platé and V. P. Shibaev, J. Poly. Sci. Macromolecular Revs., 8, p 117 to 253 (1974).

Advantageously, the comb polymer is a homopolymer having side chains  
35 containing at least 6, and preferably at least 10, carbon atoms or a copolymer having at least 25 and preferably at least 40, more preferably at least 50, molar

per cent of units having side chains containing at least 6, and preferably at least 10, carbon atoms.

As examples of preferred comb polymers there may be mentioned those of the  
 5 general formula



- where
- |    |                 |   |  |
|----|-----------------|---|--|
| 10 | D               | = | R <sup>11</sup> , COOR <sup>11</sup> , OCOR <sup>11</sup> , R <sup>12</sup> COOR <sup>11</sup> or OR <sup>11</sup> |
|    | E               | = | H, CH <sub>3</sub> , D or R <sup>12</sup>  |
|    | G               | = | H or D   |
|    | J               | = | H, R <sup>12</sup> , R <sup>12</sup> COOR <sup>11</sup> , or an aryl or heterocyclic group                         |
|    | K               | = | H, COOR <sup>12</sup> , OCOR <sup>12</sup> , OR <sup>12</sup> or COOH  |
|    | L               | = | H, R <sup>12</sup> , COOR <sup>12</sup> , OCOR <sup>12</sup> or aryl   |
| 15 | R <sup>11</sup> | ≥ | C <sub>10</sub> hydrocarbyl  |
|    | R <sup>12</sup> | ≥ | C <sub>1</sub> hydrocarbyl   |

and m and n represent mole ratios, m being within the range of from 1.0 to 0.4, n being in the range of from 0 to 0.6. R<sup>11</sup> advantageously represents a  
 20 hydrocarbyl group with from 10 to 30 carbon atoms, and R<sup>12</sup> advantageously represents a hydrocarbyl group with from 1 to 30 carbon atoms.

The comb polymer may contain units derived from other monomers if desired or required. It is within the scope of the invention to include two or more different  
 25 comb copolymers.

These comb polymers may be copolymers of maleic anhydride or fumaric acid and another ethylenically unsaturated monomer, e.g. an α-olefin or an unsaturated ester, for example, vinyl acetate. It is preferred but not essential that  
 30 equimolar amounts of the comonomers be used although molar proportions in the range of 2 to 1 and 1 to 2 are suitable. Examples of olefins that may be copolymerized with e.g. maleic anhydride, include 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, and 1-octadecene.

The copolymer may be esterified by any suitable technique and although preferred it is not essential that the maleic anhydride or fumaric acid be at least 50% esterified. Examples of alcohols which may be used include n-decan-1-ol, n-dodecan-1-ol, n-tetradecan-1-ol, n-hexadecan-1-ol, and n-octadecan-1-ol.

- 5 The alcohols may also include up to one methyl branch per chain, for example, 1-methylpentadecan-1-ol, 2-methyltridecan-1-ol. The alcohol may be a mixture of normal and single methyl branched alcohols. It is preferred to use pure alcohols rather than the commercially available alcohol mixtures but if mixtures are used the  $R^{12}$  refers to the average number of carbon atoms in the alkyl group; if alcohols that contain a branch at the 1 or 2 positions are used  $R^{12}$  refers to the straight chain backbone segment of the alcohol.
- 10

- These comb polymers may especially be fumarate or itaconate polymers and copolymers such as for example those described in European Patent Applications 153 176, 153 177 and 225 688, and WO 91/16407.
- 15

- Particularly preferred fumarate comb polymers are copolymers of alkyl fumarates and vinyl acetate, in which the alkyl groups have from 12 to 20 carbon atoms, more especially polymers in which the alkyl groups have 14 carbon atoms or in which the alkyl groups are a mixture of  $C_{14}/C_{16}$  alkyl groups, made, for example, by solution copolymerizing an equimolar mixture of fumaric acid and vinyl acetate and reacting the resulting copolymer with the alcohol or mixture of alcohols, which are preferably straight chain alcohols. When the mixture is used it is advantageously a 1:1 by weight mixture of normal  $C_{14}$  and  $C_{16}$  alcohols.
- 20
- 25 Furthermore, mixtures of the  $C_{14}$  ester with the mixed  $C_{14}/C_{16}$  ester may advantageously be used. In such mixtures, the ratio of  $C_{14}$  to  $C_{14}/C_{16}$  is advantageously in the range of from 1:1 to 4:1, preferably 2:1 to 7:2, and most preferably about 3:1, by weight. The particularly preferred fumarate comb polymers may, for example, have a number average molecular weight in the range of 1,000 to 100,000, preferably 1,000 to 30,000, as measured by Vapour Phase Osmometry (VPO).
- 30

- Other suitable comb polymers are the polymers and copolymers of  $\alpha$ -olefins and esterified copolymers of styrene and maleic anhydride, and esterified copolymers of styrene and fumaric acid; mixtures of two or more comb polymers may be used in accordance with the invention and, as indicated above, such use may be advantageous.
- 35

## (ii) Polyoxyalkylene Compounds

Examples are polyoxyalkylene esters, ethers, ester/ethers and mixtures thereof,  
 5 particularly those containing at least one, preferably at least two C<sub>10</sub> to C<sub>30</sub>  
 linear saturated alkyl groups and a polyoxyalkylene glycol group of molecular  
 weight up to 5,000 preferably 200 to 5,000, the alkyl group in said  
 polyoxyalkylene glycol containing from 1 to 4 carbon atoms. These materials  
 form the subject of European Patent Publication 0 061 895 A2. Other such  
 10 additives are described in United States Patent 4 491 455.

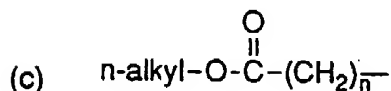
The preferred esters, ethers or ester/ethers which may be used may be  
 structurally depicted by the formula



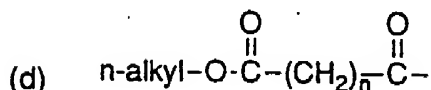
where R<sup>3</sup> and R<sup>4</sup> are the same or different and may be

(a) n-alkyl

20



25



n being, for example, 1 to 30, the alkyl group being linear and saturated and  
 containing 10 to 30 carbon atoms, and A representing the polyalkylene segment  
 of the glycol in which the alkylene group has 1 to 4 carbon atoms, such as a  
 30 polyoxymethylene, polyoxyethylene or polyoxytrimethylene moiety which is  
 substantially linear; some degree of branching with lower alkyl side chains (such  
 as in polyoxypropylene glycol) may be present but it is preferred that the glycol is  
 substantially linear. A may also contain nitrogen.

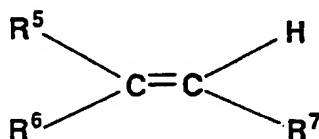
Examples of suitable glycols are substantially linear polyethylene glycols (PEG) and polypropylene glycols (PPG) having a molecular weight of about 100 to 5,000, preferably about 200 to 2,000. Esters are preferred and fatty acids containing from 10-30 carbon atoms are useful for reacting with the glycols to form the ester additives, it being preferred to use a C<sub>18</sub>-C<sub>24</sub> fatty acid, especially behenic acid. The esters may also be prepared by esterifying polyethoxylated fatty acids or polyethoxylated alcohols.

Polyoxyalkylene diesters, diethers, ether/esters and mixtures thereof are suitable as additives, diesters being preferred for use in narrow boiling distillates when minor amounts of monoethers and monoesters (which are often formed in the manufacturing process) may also be present. It is important for additive performance that a major amount of the dialkyl compound is present. In particular, stearic or behenic diesters of polyethylene glycol, polypropylene glycol or polyethylene/polypropylene glycol mixtures are preferred.

Other examples of polyoxyalkylene compounds are those described in Japanese Patent Publication Nos 2-51477 and 3-34790 (both Sanyo), and the esterified alkoxyated amines described in EP-A-117,108 and EP-A-326,356 (both Nippon Oil and Fats).

### (iii) Ethylene/Unsaturated Ester Copolymers

Ethylene copolymer flow improvers have a polymethylene backbone divided into segments by oxyhydrocarbon side chains, i.e. ethylene unsaturated ester copolymer flow improvers. The unsaturated monomers copolymerisable with ethylene to form the copolymers include unsaturated mono and diesters of the general formula:



wherein R<sup>5</sup> represents hydrogen or a methyl group;

R<sup>6</sup> represents a -OOCR<sup>8</sup> or -COOR<sup>8</sup> group wherein R<sup>8</sup> represents hydrogen or a C<sub>1</sub> to C<sub>28</sub>, preferably C<sub>1</sub> to C<sub>16</sub>, more preferably a C<sub>1</sub> to C<sub>8</sub>, straight or branched

chain alkyl group, provided that  $R^8$  does not represent hydrogen when  $R^6$  represents  $-\text{COOR}^8$ ; and  $R^7$  is hydrogen or  $-\text{COOR}^8$ .

- 5 The monomer, when  $R^6$  and  $R^7$  are hydrogen and  $R^5$  is  $-\text{OOCR}^8$ , includes vinyl alcohol esters of  $C_1$  to  $C_{29}$ , preferably  $C_1$  to  $C_5$ , monocarboxylic acids, and preferably  $C_2$  to  $C_{29}$ , more preferably  $C_1$  to  $C_5$  monocarboxylic acids, most preferably  $C_2$  to  $C_5$  monocarboxylic acids. Examples of vinyl esters which may be copolymerised with ethylene include vinyl acetate, vinyl propionate and vinyl butyrate or isobutyrate, vinyl acetate and vinyl propionate being preferred.
- 10 Preferably, the copolymers contain from 5 to 40 wt% of the vinyl ester, more preferably from 10 to 35 wt% vinyl ester [change to molar]. They may also be in the form of mixtures of two copolymers such as those described in US Patent 3,961,916. Preferably, number average molecular weight, as measured by
- 15 vapour phase osmometry, of the copolymer is 1,000 to 10,000, more preferably 1,000 to 5,000. If desired, the copolymers may be derived from additional comonomers, e.g. they may be terpolymers or tetrapolymers or higher polymers, for example where the additional comonomer is isobutylene or diisobutylene.
- 20 Such copolymers may also be made by transesterification, or by hydrolysis and re-esterification, of an ethylene unsaturated ester copolymer to give a different ethylene unsaturated ester copolymer. For example, ethylene vinyl hexanoate and ethylene vinyl octanoate copolymers may be made in this way, e.g. from an ethylene vinyl acetate copolymer.

25

#### (iv) Polar Organic, Nitrogen-containing Compounds

- The oil-soluble polar nitrogen compound is either ionic or non-ionic and is capable of acting as a wax crystal growth inhibitor in fuels. It comprises for
- 30 example one or more of the compounds (a) to (c) as follows:

- (a) An amine salt and/or amide formed by reacting at least one molar proportion of a hydrocarbyl substituted amine with a molar proportion of a hydrocarbyl acid having 1 to 4 carboxylic acid groups or its anhydride.

35

Ester/amides may be used containing 30 to 300, preferably 50 to 150 total carbon atoms. These nitrogen compounds are described in US Patent

4 211 534: Suitable amines are usually long chain C<sub>12</sub>-C<sub>40</sub> primary,<sup>\*</sup> secondary, tertiary or quaternary amines or mixtures thereof but shorter chain amines may be used provided the resulting nitrogen compound is oil soluble and therefore normally contains about 30 to 300 total carbon  
5 atoms. The nitrogen compound preferably contains at least one straight chain C<sub>8</sub> to C<sub>40</sub>, preferably C<sub>14</sub> to C<sub>24</sub>, alkyl segment.

Suitable amines include primary, secondary, tertiary or quaternary, but preferably are secondary. Tertiary and quaternary amines can only form  
10 amine salts. Examples of amines include tetradecyl amine, cocoamine, and hydrogenated tallow amine. Examples of secondary amines include dioctadecyl amine and methyl-behenyl amine. Amine mixtures are also suitable such as those derived from natural materials. A preferred amine  
15 is a secondary hydrogenated tallow amine of the formula HNR<sup>9</sup>R<sup>10</sup> wherein R<sup>9</sup> and R<sup>10</sup> are alkyl groups derived from hydrogenated tallow fat composed of approximately 4% C<sub>14</sub>, 31% C<sub>16</sub>, 59% C<sub>18</sub>.

Examples of suitable carboxylic acids and their anhydrides for preparing the nitrogen compounds include cyclohexane 1,2 dicarboxylic acid,  
20 cyclohexene 1,2 dicarboxylic acid, cyclopentane 1,2 dicarboxylic acid and naphthalene dicarboxylic acid, and 1,4-dicarboxylic acids including dialkyl spirobis lactone. Generally, these acids have about 5-13 carbon atoms in the cyclic moiety. Preferred acids useful in the present invention are benzene dicarboxylic acids such as phthalic acid, isophthalic acid,  
25 and terephthalic acid. Phthalic acid or its anhydride is particularly preferred. The particularly preferred compound is the amide-amine salt formed by reacting 1 molar portion of phthalic anhydride with 2 molar portions of dihydrogenated tallow amine. Another preferred compound is the diamide formed by dehydrating this amide-amine salt.

30 Other examples are long chain alkyl or alkylene substituted dicarboxylic acid derivatives such as amine salts of monoamides of substituted succinic acids, examples of which are known in the art and described in US-A-4 147 520, for example. Suitable amines may be those described  
35 above.

Other examples are condensates such as described in EP-A-327,423.

- (b) A chemical compound comprising or including a cyclic ring system, the compound carrying at least two substituents of the general formula (I) below on the ring system

5



where A is an aliphatic hydrocarbyl group that is optionally interrupted by one or more hetero atoms and that is straight chain or branched, and R<sup>13</sup> and R<sup>14</sup> are the same or different and each is independently a hydrocarbyl group containing 9 to 40 carbon atoms optionally interrupted by one or more hetero atoms, the substituents being the same or different and the compound optionally being in the form of a salt thereof.

Preferably, A has from 1 to 20 carbon atoms and is preferably a methylene or polymethylene group.

Examples of substituted hydrocarbyl groups include 2-hydroxyethyl, 3-hydroxypropyl, 4-hydroxybutyl, 2-ketopropyl, ethoxyethyl, and propoxypropyl. The groups may also or alternatively contain atoms other than carbon in a chain or ring otherwise composed of carbon atoms. Suitable hetero atoms include, for example, nitrogen, sulphur, and, preferably, oxygen.

The cyclic ring system may include homocyclic, heterocyclic, or fused polycyclic assemblies, or a system where two or more such cyclic assemblies are joined to one another and in which the cyclic assemblies may be the same or different. Where there are two or more such cyclic assemblies, the substituents of the general formula (I) may be on the same or different assemblies, preferably on the same assembly. Preferably, the or each cyclic assembly is aromatic, more preferably a benzene ring. Most preferably, the cyclic ring system is a single benzene ring when it is preferred that the substituents are in the ortho or meta positions, which benzene ring may be optionally further substituted.

35



The ring atoms in the cyclic assembly or assemblies are preferably carbon atoms but may for example include one or more ring N, S or O atom, in which case or cases the compound is a heterocyclic compound.

5        Examples of such polycyclic assemblies include:

- (i) condensed benzene structures such as naphthalene, anthracene, phenanthrene, and pyrene;
- 10        (ii) condensed ring structures where none of or not all of the rings are benzene such as azulene, indene, hydroindene, fluorene, and diphenylene oxide;
- (iii) rings joined "end-on" such as diphenyl;
- 15        (iv) heterocyclic compounds such as quinoline, indole, 2:3 dihydroindole, benzofuran, coumarin, isocoumarin, benzothiophen, carbazole and thiodiphenylamine;
- 20        (v) non-aromatic or partially saturated ring systems such as decalin (i.e. decahydronaphthalene),  $\alpha$ -pinene, cardinene, and bornylene; and
- (vi) three-dimensional structures such as norbornene, bicycloheptane  
25        (i.e. norbornane), bicyclooctane, and bicyclooctene.

Each hydrocarbyl group constituting R<sup>13</sup> and R<sup>14</sup> in the invention (Formula I) may for example be an alkyl or alkylene group or a mono- or  
30        poly-alkoxyalkyl group. Preferably, each hydrocarbyl group is a straight chain alkyl group. The number of carbon atoms in each hydrocarbyl group is preferably 16 to 40, more preferably 16 to 24.

Also, it is preferred that the cyclic system is substituted with only two substituents of the general formula (I) and that A is a methylene group.

35

Examples of salts of the chemical compounds are the acetate and the hydrochloride.

The compounds may conveniently be made by reducing the corresponding amide which may be made by reacting a secondary amine with the appropriate acid chloride; and

5

- (c) A condensate of long chain primary or secondary amine with a carboxylic acid-containing polymer.

10

Specific examples include polymers such as described in GB-A-2,121,807, FR-A-2,592,387 and DE-A-3,941,561; and also esters of telemer acid and alkanoloamines such as described in US-A-4,639,256; a long chain epoxide/amine reaction product which may optionally be further reacted with a polycarboxylic acid; and the reaction product of an amine containing a branched carboxylic acid ester, an epoxide and a

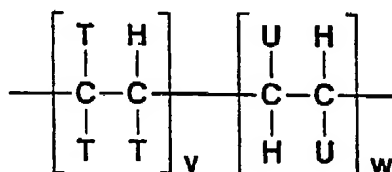
15

mono-carboxylic acid polyester such as described in US-A-4,631,071.

#### (v) Hydrocarbon Polymers

Examples are those represented by the following general formula

20



where T = H or R<sup>15</sup>

U = H, T or aryl

25

R<sup>15</sup> = C<sub>1</sub>-C<sub>30</sub> hydrocarbyl

and v and w represent mole ratios, v being within the range 1.0 to 0.0, w being within the range 0.0 to 1.0.

30

These polymers may be made directly from ethylenically unsaturated monomers or indirectly by hydrogenating the polymer made from monomers such as isoprene and butadiene.

Preferred hydrocarbon polymers are copolymers of ethylene and at least one  $\alpha$ -olefin, having a number average molecular weight of at least 30,000. Preferably the  $\alpha$ -olefin has at most 20 carbon atoms. Examples of such olefins are propylene, 1-butene, isobutene, n-octene-1, isooctene-1, n-decene-1, and n-dodecene-1. The copolymer may also comprise small amounts, e.g. up to 10% by weight of other copolymerizable monomers, for example olefins other than  $\alpha$ -olefins, and non-conjugated dienes. The preferred copolymer is an ethylene-propylene copolymer. It is within the scope of the invention to include two or more different ethylene- $\alpha$ -olefin copolymers of this type.

The number average molecular weight of the ethylene- $\alpha$ -olefin copolymer is, as indicated above, at least 30,000, as measured by gel permeation chromatography (GPC) relative to polystyrene standards, advantageously at least 60,000 and preferably at least 80,000. Functionally no upper limit arises but difficulties of mixing result from increased viscosity at molecular weights above about 150,000, and preferred molecular weight ranges are from 60,000 and 80,000 to 120,000.

Advantageously, the copolymer has a molar ethylene content between 50 and 85 per cent. More advantageously, the ethylene content is within the range of from 57 to 80%, and preferably it is in the range from 58 to 73%; more preferably from 62 to 71%, and most preferably 65 to 70%.

Preferred ethylene- $\alpha$ -olefin copolymers are ethylene-propylene copolymers with a molar ethylene content of from 62 to 71% and a number average molecular weight in the range 60,000 to 120,000, especially preferred copolymers are ethylene-propylene copolymers with an ethylene content of from 62 to 71% and a molecular weight from 80,000 to 100,000.

The copolymers may be prepared by any of the methods known in the art, for example using a Ziegler type catalyst. Advantageously, the polymers are substantially amorphous, since highly crystalline polymers are relatively insoluble in fuel oil at low temperatures.

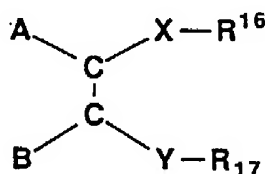
The additive composition may also comprise a further ethylene- $\alpha$ -olefin copolymer, advantageously with a number average molecular weight of at most 7500, advantageously from 1,000 to 6,000, and preferably from 2,000 to 5,000,

as measured by vapour phase osmometry. Appropriate  $\alpha$ -olefins are as given above, or styrene, with propylene again being preferred. Advantageously the ethylene content is from 60 to 77 molar per cent although for ethylene-propylene copolymers up to 86 molar per cent by weight ethylene may be employed with advantage.

Examples of hydrocarbon polymers are described in WO-A-9 111 488.

#### (vi) Sulphur Carboxy Compounds

Examples are those described in EP-A-0,261,957 which describes the use of compounds of the general formula



in which  $-\text{Y}-\text{R}^{17}$  is  $\text{SO}_3^{(-)(+)}\text{NR}_3^{18}\text{R}^{17}$ ,  $-\text{SO}_3^{(-)(+)}\text{HNR}_2^{18}\text{R}^{17}$ ,

$-\text{SO}_3^{(-)(+)}\text{H}_2\text{NR}^{18}\text{R}^{17}$ ,  $-\text{SO}_3^{(-)(+)}\text{H}_3\text{NR}^{17}$ ,

$-\text{SO}_2\text{NR}^{18}\text{R}^{17}$  or  $-\text{SO}_3\text{R}^{17}$ ;

$-\text{X}-\text{R}^{16}$  is  $-\text{Y}-\text{R}^{17}$  or  $-\text{CONR}^{18}\text{R}^{16}$ ,

$-\text{CO}_2^{(-)(+)}\text{NR}_3^{18}\text{R}^{16}$ ,  $-\text{CO}_2^{(-)(+)}\text{HNR}_2^{18}\text{R}^{16}$ ,

$-\text{R}^{19}-\text{COOR}^{16}$ ,  $-\text{NR}^{18}\text{COR}^{16}$ ,

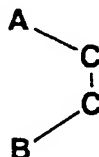
$-\text{R}^{19}\text{OR}^{16}$ ,  $-\text{R}^{19}\text{OCOR}^{16}$ ,  $-\text{R}^{19}, \text{R}^{16}$ ,

$-\text{N}(\text{COR}^{18})\text{R}^{16}$  or  $\text{Z}^{(-)(+)}\text{NR}_3^{18}\text{R}^{16}$ ;

$-\text{Z}^{(-)}$  is  $\text{SO}_3^{(-)}$  or  $-\text{CO}_2^{(-)}$ ;

$\text{R}^{16}$  and  $\text{R}^{17}$  are alkyl, alkoxyalkyl or polyalkoxyalkyl containing at least 10 carbon atoms in the main chain;

$\text{R}^{18}$  is hydrocarbyl and each  $\text{R}^{18}$  may be the same or different and  $\text{R}^{19}$  is absent or is  $\text{C}_1$  to  $\text{C}_5$  alkylene and in



the carbon-carbon (C-C) bond is either a) ethylenically unsaturated when A and  
5 B may be alkyl, alkenyl or substituted hydrocarbyl groups or b) part of a cyclic  
structure which may be aromatic, polynuclear aromatic or cyclo-aliphatic, it is  
preferred that X-R<sup>16</sup> and Y-R<sup>17</sup> between them contain at least three alkyl,  
alkoxyalkyl or polyalkoxyalkyl groups.

#### 10 (vii) Hydrocarbylated-Aromatics

These materials are condensates comprising aromatic and hydrocarbyl parts.  
The aromatic part is conveniently an aromatic hydrocarbon which may be  
unsubstituted or substituted with, for example, non-hydrocarbon substituents.  
15 Such aromatic hydrocarbon preferably contains a maximum of these substituent  
groups and/or three condensed rings, and is preferably naphthalene. The  
hydrocarbyl part is a hydrogen and carbon containing part connected to the rest  
of the molecule by a carbon atom. It may be saturated or unsaturated, and  
straight or branched, and may contain one or more hetero-atoms provided they  
20 do not substantially affect the hydrocarbyl nature of the part. Preferably the  
hydrocarbyl part is an alkyl part, conveniently having more than 8 carbon atoms.  
The molecular weight of such condensates may, for example, be in the range of  
2,000 to 200,000 such as 2,000 to 20,000, preferably 2,000 to 8,000. Examples  
are known in the art, primarily as lube oil pour depressants and as dewaxing  
25 aids as mentioned hereinbefore, they may, for example, be made by condensing  
a halogenated wax with an aromatic hydrocarbon. More specifically, the  
condensation may be a Friedel-Crafts condensation where the halogenated wax  
contains 15 to 60, e.g. 16 to 50, carbon atoms, has a melting point of about 200  
to 400°C and has been chlorinated to 5 to 25 wt% chlorine, e.g. 10 to 18 wt%.  
30 Another way of making similar condensates may be from olefins and the  
aromatic hydrocarbons.

Multicomponent additive systems may be used and the ratios of additives to be  
used will depend on the fuel to be treated.

Middle distillate fuel oils may contain one or more other additives. Particularly noteworthy additives are the ashless dispersants which are described in numerous patent specifications, such as EP-A-0 482 253. Further examples  
5 include macrocyclic ashless dispersants, cetane improvers, polymers of monoolefins, metallic-based combustion improvers such as ferrocene, corrosion inhibitors, anti-oxidants, reodorants, and antiwear additives.

In accordance with all use and liquid composition aspects, the quantity of  
10 reaction product in the liquid is usually in excess of 0.00005% (weight of additive per weight of organic liquid).

The maximum quantity employed does not appear to be critical, appearing in practice to be governed by economics and choice. However, particularly  
15 suitable quantities lie in the range of 0.00005% to 5.0% weight of product per weight of organic liquid. More preferably, the product may be employed in the range 0.0001% to 0.5%, more preferably still 0.0005% to 0.1%, and most preferably 0.0005% to 0.01% weight per weight of fuel.

The reaction products may be introduced into the organic liquids in the form of a concentrate. In such a concentrate, the product(s) may be dissolved in a solvent at a concentration within wide limits according to the needs and restrictions of the specific application, for example from 1:90, such as 10:80, per cent (weight:weight). Examples of suitable solvents are hydrocarbons or oxygen-  
25 containing hydrocarbons such as kerosene, aromatic naphthas, and mineral lubricating oils. Optionally, co-additives such as those earlier described may be present, depending upon the organic liquid to be treated and the demands of each circumstance.

30 The various aspects of the invention will now be illustrated by way of example only as follows.

## EXAMPLES OF REACTION PRODUCTS

### Example 1

- 5 Oleic acid (282 g; 1.0 moles) was dissolved in toluene (250 mls). Diethylene triamine (DETA) (34.3 g; 0.33 moles) was dissolved in toluene (100 mls), the slight stoichiometric excess of oleic acid being used to ensure subsequent acylation of every amino group. The amine solution was added slowly to the stirred solution of the acid over one hour. During this addition there was an
- 10 exotherm and the reaction temperature increased by 13°C. When the addition of the amine was complete, the reaction mixture was heated to reflux for 7 hours and 45 minutes. During the reflux water (17 mls; theory = 18 mls) was collected in a Dean & Stark trap. At the end of the reflux the toluene was removed by distilling the reaction mixture to a pot temperature of 150°C. Final
- 15 traces of solvent were removed from the product by applying a vacuum of 500 mm Hg.

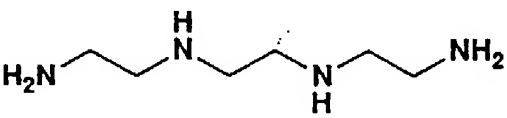
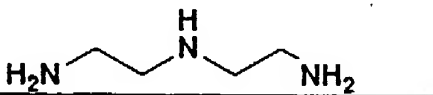
The product obtained was a waxy solid. The IR spectrum of the product showed no trace of oleic acid (peak at 1711 wavenumbers). There were, however,

20 peaks at 1665 and 1590 wavenumbers consistent with the formation of secondary and tertiary amide groups, i.e. that acylation had been essentially full.

### Examples 2 and 3

- 25 Analogous reaction conditions were employed to generate fully-acylated reaction products as illustrated in Table I below.

Table I

Ex. No	Reactants		Ratio of a:b used
	(a) polyamine	(b) monocarboxylic acylating agent	
2		oleic acid	slightly greater than 1:4
3		tall-oil fatty acid	slightly greater than 1:3

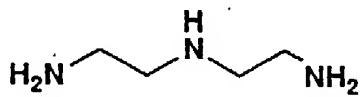
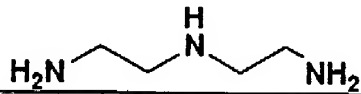
## Examples 4 and 5

5

Reaction conditions analogous to those used for the synthesis of the previous examples 1-3 were employed in the reaction of one mole of diethylene triamine with two moles of monocarboxylic acylating agent, as shown in Table II.

10

Table II

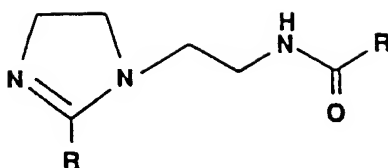
Example No	Reactants	
	(a) polyamine	(b) monocarboxylic acylating agent
4		stearic acid
5		tall-oil fatty acid

In both examples, the major product was of the form

15



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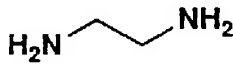
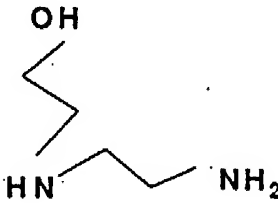


- where the acylating agent (b) corresponds to RCOOH, i.e. still a fully-acylated product within the meaning of this specification, every amino group of the
- 5 polyamine having undergone reaction upon addition of acylating agent (b) and three moles of water per mole of DETA having been evolved.

#### Examples 6 to 14

- 10 Reaction conditions analogous to those used for the synthesis of Examples 1-3 were employed to generate products according to the use and liquid composition aspects of the invention, as illustrated in Table III below.

Table III

Example No	Reactants	
	(a) polyamine	(b) monocarboxylic acylating agent
6		stearic acid
7		oleic acid
8		ceanoic acid
9		coco fatty acid
10		tall-oil fatty acid
11		1:1 mixture of coco and tall-oil fatty acids
12		coco fatty acid
13		ceanoic acid
14		stearic acid

In each example, one mole of polyamine was reacted with slightly in excess of two moles of acylating agent.

#### Examples of Use and Liquid Composition Aspects

Examples 1-14 were tested for their effects on the foaming tendencies of organic liquids.

- In the following Experiments A, B and C the procedure used to assess foaming tendency involved the hand-shaking of 100 ml of test liquid in a previously-cleaned and dried 4 oz bottle, the bottle then being placed in normal attitude on a stationary, flat surface. The subsequent length of time (in seconds) over which the foam generated by shaking collapsed sufficiently to reveal a clear area of liquid surface was recorded as a measure of foaming tendency, longer foam collapse times indicating greater foam stability.

### Experiment A

10

For the purposes of this experiment, two conventional European diesel fuels showing a pronounced tendency to foam were selected as suitable organic liquids. Each diesel fuel possessed the following characteristics:

### 15 Diesel Fuel V

Test Description	Method/Designation	Result
PAAR Density	D4052/IP365	0.8399
KV 40C	D445/IP71	2.825
Cloud Point	IP219/D2500 (auto)	-6°C
Pour Point	D97/IP15	-27°C
Sulphur %wt	XRF RD/86/10	0.20

	Distillation:	Vol% Off	Temp °C
	by D86/IP123	IBP	148
5	method	5	194
		10	209
		20	229
		30	248
		40	263
10		50	275
		60	286
		70	298
		80	312
		90	331
15		95	345
		FBP	367

**Diesel Fuel W**

A conventional European diesel fuel of similar characteristics to fuel V.

- 20 Previously-exemplified reaction products were added to samples of each test fuel, foam collapse times after 30 seconds of shaking being measured in accordance with the prescribed method and shown in Table IV below.

Table IV

Additive Example No		Foam Collapse Time (s) of Test Fuel @ given additive treat-rate			
		0	0.001% (w/w)	0.002% (w/w)	0.003% (w/w)
Base Fuel	V	32	-	-	-
	W	53	-	-	-
3			24	28	27
			-	-	-
5			6	-	-
			11	-	-
7			21	41	32
			62	-	-
8			21	26	25
			58	-	-
11			7	7	6
			8	-	-
12			26	-	10
			-	-	-
14			24	-	17
			-	-	-

- 5 For each reaction product, the first figure in a given column indicates foam collapse time in diesel fuel V, the second figure the time in diesel fuel W. All figures are the average of two tests. The character '-' indicates an untested combination of fuel and reaction product.

**Experiment B**

The effect of Example 6 on the foam-collapse time of two further diesel fuels X and Y, similar in characteristics to fuels V and W previously described, was compared with a proprietary organo-silicon block copolymer of the class hereinbefore described, known to be effective in reducing the foaming tendency of diesel fuels, and referred to as Comparative Example A.

Example 6 was added to each fuel as part of a proprietary additive Concentrate C of specific gravity 0.89. Concentrate C contained 4.5% volume of Example 6, in admixture with further additives and diluent.

Within this concentrate, only Example 6 is believed to exhibit a significant effect on fuel foaming tendency.

The results of this testing are shown in the Figures 1 and 2 attached.

**Experiment C**

The effect of Examples 1 and 2 on the foam-collapse time of a fifth diesel fuel Z, also similar in characteristics to fuels V and W previously described, was measured using the prescribed test, modified such that the shaking period was shortened to 15 seconds. The results are shown below in Table V.

**Table V**

Additive Example No	Foam Collapse Time (s) of Test Fuel @ given additive treat-rate		
	0	0.001% (w/w)	0.005% (w/w)
Base Fuel Z	56	-	-
1	-	20	19
2	-	37	28

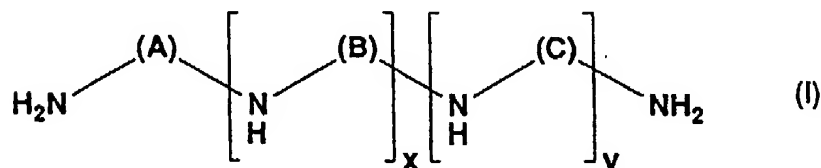
All results are the average of two tests. As before the character '-' indicates an untested combination.

- The additives of this invention are thus effective as inhibitors of the foaming tendencies of organic liquids, particularly petroleum fuels. In addition, their silicon-free composition precludes the formation and emission of particles of silicon oxides upon combustion; moreover, the absence of other ash-producing
- 5 elements ensures that their contribution to particulate emissions will be negligible.

**Claims:**

1. The use, for suppression or inhibition of the foaming tendencies of an organic liquid, of a product obtainable by the reaction between

- (a) a polyamine of the formula (I)



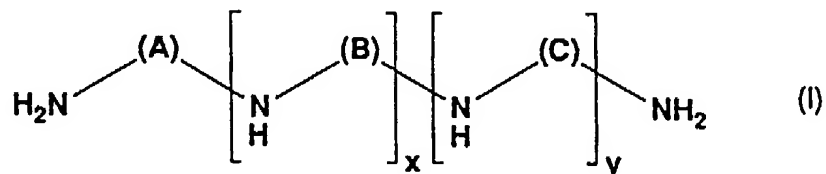
wherein A, B and C are the same or different and each represents a hydrocarbyl group, and x and y are integers whose sum is in the range from 0 to 10, and

- (b) a carboxylic acylating agent

provided that, when the sum of x and y is 0 and (b) is selected from the group consisting of stearoyl, palmitoyl, myristoyl, lauroyl and oleoyl acylating agents, A does not represent ethylene or trimethylene.

2. The use, for suppression or inhibition of the foaming tendencies of an organic liquid, of a product obtainable by the reaction between

- (a) a polyamine of the formula (I)



wherein A, B and C are the same or different and each represents a hydrocarbyl group, and x and y are integers whose sum is in the range from 1 to 10, and

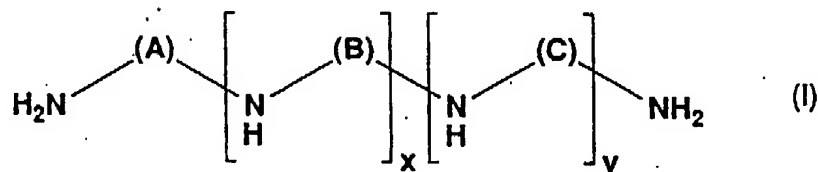
- (b) a carboxylic acylating agent



3. The use according to claim 1 or claim 2 wherein said product is formed by the reaction between one mole of the polyamine and at least two moles of the carboxylic acylating agent.
- 5 4. The use according to any of the preceding claims wherein said product is formed by the complete acylation of the polyamine by the carboxylic acylating agent.
- 10 5. The use according to any of claims 1 to 4 wherein acylating agent (b) is a monocarboxylic acylating agent of the formula (II)
- $$\begin{array}{c} \text{O} \\ \parallel \\ \text{R} - \text{C} - \text{X} \end{array} \quad (\text{II})$$
- wherein R represents a hydrocarbyl group, and X represents a leaving group.
- 15 6. The use according to claim 5 wherein the monocarboxylic acylating agent comprises a fatty acid composition.
- 20 7. The use according to claim 5 or claim 6 wherein R represents a hydrocarbyl group containing from 10 to 30 carbon atoms.
8. The use according to any of claims 5 to 7 wherein R represents a straight chain alkyl group.
- 25 9. The use according to any of the preceding claims wherein the polyamine is a polyalkylene polyamine.
- 30 10. The use according to any of claims 5 to 9 wherein said product is formed by the reaction between a polyalkylene polyamine and a monocarboxylic acylating agent selected from the group comprising cecanoic acid and coco-fatty acid fraction, or mixtures thereof.
- 35 11. The use according to any one of the preceding claims wherein said product is present in the organic liquid in the concentration range of 0.00005 to 5.0% wt per weight of liquid.

12. The use according to any one of the preceding claims wherein said organic liquid is a hydrocarbon fuel.
- 5 13. The use according to claim 12 wherein said hydrocarbon fuel is a middle distillate fuel.
14. A liquid composition comprising a major proportion of an organic liquid, and a minor proportion of an additive comprising a fully-acylated product of reaction  
10 between

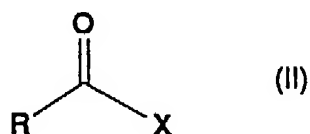
(a) a polyamine of the formula (I)



15

wherein A, B and C are the same or different and each represents a hydrocarbyl group, and x and y are integers whose sum is in the range from 0 to 10, and

20 (b) a monocarboxylic acylating agent of the formula (II)



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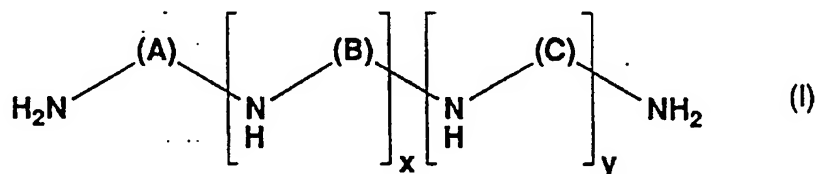
wherein R represents a hydrocarbyl group, and X represents a leaving group, provided that (b) is not phenylstearic acid, isostearic acid or tall-oil fatty acid,

30

provided that, when the sum of x and y is 0 and R is selected from the group consisting of n-heptadecyl, n-hexadecyl, n-tetradecyl, n-dodecyl and cis-9-heptadecenyl, A does not represent ethylene or trimethylene.

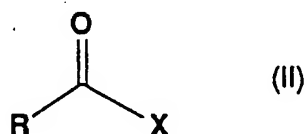
15. The liquid composition according to claim 14 wherein the sum of x and y is in the range from 1 to 10.
16. An liquid composition according to claim 14 or claim 15 wherein said organic liquid is a hydrocarbon fuel.
17. A liquid composition according to claim 16 wherein said liquid hydrocarbon fuel is a middle distillate fuel.
18. A fully-acylated product of reaction between:

- (a) a polyamine of the formula (I)



wherein A, B and C may be the same or different and each represents a hydrocarbyl group, and x and y are integers whose sum is in the range from 1 to 10, and

- (b) a monocarboxylic acylating agent of the formula (II)



wherein R represents a hydrocarbyl group, and X represents a leaving group, provided that (b) is not phenylstearic acid, isostearic acid or tall-oil fatty acid.

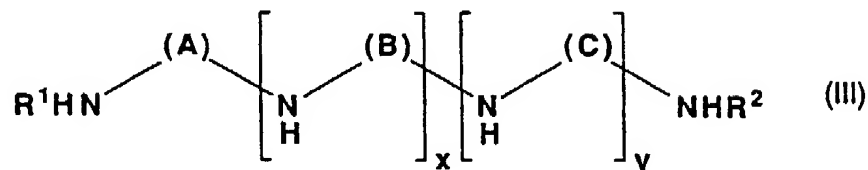
19. The liquid composition according to any of claims 14 to 17, or the product according to claim 18, wherein R represents a hydrocarbyl group containing from 10 to 30 carbon atoms.

20. The liquid composition, or product, according to claim 19 wherein R represents a straight chain alkyl group.

21. A fully-acylated product of reaction between:

5

(a) a polyamine of the formula (III)

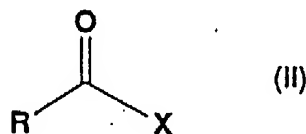


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wherein A, B and C may be the same or different and each represents a hydrocarbyl group, and x and y are integers whose sum is in the range from 0 to 10, and wherein R<sup>1</sup> and R<sup>2</sup> may be the same or different and each represents hydrogen or a hydrocarbyl group, provided that both R<sup>1</sup> and R<sup>2</sup> are not hydrogen, and

15

(b) a monocarboxylic acylating agent of the formula (II)



20

wherein R represents a hydrocarbyl group, and X represents a leaving group.

22. A liquid composition a major proportion of an organic liquid, and a minor proportion of an additive comprising the product of claim 21.

25

23. The use, for suppression of inhibition of the foaming tendencies of an organic liquid, of the product of claim 21.

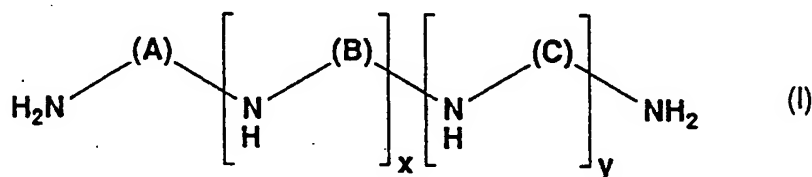
24. The product, liquid composition or use according to any of claims 21 to 23 wherein R<sup>1</sup> and R<sup>2</sup> each independently represent hydrogen or an aliphatic hydrocarbyl group.

30

25. The product, liquid composition or use according to claim 24 wherein the aliphatic hydrocarbyl group is an alkyl, oxyalkyl or hydroxyalkyl group.

5 26. The use, for suppression or inhibition of the foaming tendencies of an organic liquid, of an additive comprising both a product obtainable by the reaction between

(a) a polyamine of the formula (I)



wherein A, B and C are the same or different and each represents a hydrocarbyl group, and x and y are integers whose sum is in the range from 0 to 10, and

15 (b) a carboxylic acylating agent,

and one or more low temperature flow improving additives selected from the following

20

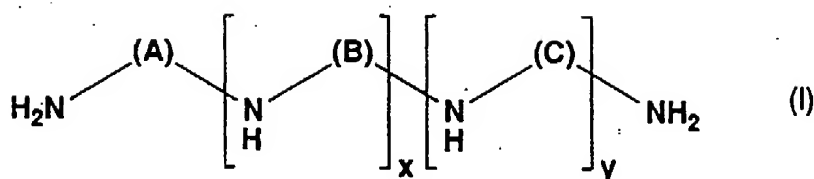
- (i) a comb polymer,
- (ii) a polyoxyalkylene ester, ether, ester/ether or a mixture thereof,
- (iii) an ethylene/unsaturated ester copolymer,
- (iv) a polar, organic, nitrogen-containing wax crystal growth inhibitor,
- 25 (v) a hydrocarbon polymer,
- (vi) sulphur carboxy compounds, and
- (vii) hydrocarbylated aromatics.

25

27. A liquid composition comprising a major proportion of an organic liquid and a minor proportion of an additive comprising both a fully acylated product of reaction between

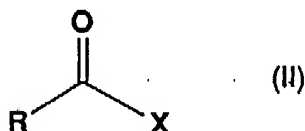
30

(a) a polyamine of the formula (I)



wherein A, B and C are the same or different and each represents a hydrocarbyl group, and x and y are integers whose sum is in the range from 0 to 10, and

(b) a monocarboxylic acylating agent of the formula (II)



wherein R represents a hydrocarbyl group, and X represents a leaving group, provided that (b) is not phenylstearic acid, isostearic acid or tall-oil fatty acid,

and one or more low temperature flow improving additives selected from the following

- (i) a comb polymer,
- (ii) a polyoxyalkylene ester, ether, ester/ether or a mixture thereof,
- (iii) an ethylene/unsaturated ester copolymer,
- (iv) a polar, organic, nitrogen-containing wax crystal growth inhibitor,
- (v) a hydrocarbon polymer,
- (vi) sulphur carboxy compounds, and
- (vii) hydrocarbylated aromatics.

## INTERNATIONAL SEARCH REPORT

Inter. Appl. No.

PCT/EP 93/02560

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 5 C10L1/2 B01D19/04 C10L1/14

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 C10L B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB,A,658 494 (SHELL) 10 October 1951	1,3-14, 16,17, 19-25 26,27
Y	see page 5, line 32 - line 54 ---	
X	FR,A,2 253 082 (E.I. DU PONT DE NEMOURS AND COMP.) 27 June 1975	14-20
Y	see page 3 - page 4 see page 7 - page 8 ---	26,27
X	EP,A,0 055 355 (BASF) 7 July 1982	14-20
Y	see page 6	26,27
A	see page 4, line 21 - line 26 ---	10
X	US,A,3 259 586 (DICKSON ET AL.) 5 July 1966 cited in the application see the whole document ---	1-25
-/--		

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Date of the actual completion of the international search

29 December 1993

Date of mailing of the international search report

13.01.94

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# INTERNATIONAL SEARCH REPORT

Int. Application No

PCT/EP 93/02560

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
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X	US,A,3 127 354 (DE GROOTE ET AL.) 31 March 1964 see the whole document ---	21-25
X	FR,A,1 584 938 (BASF) 2 January 1970 see the whole document ---	14-20
Y		1-13
P,Y	US,A,5 192 336 (GREWAL) 9 March 1993 see the whole document ---	1-13
X	US,A,2 805 135 (BELL ET AL.) 3 September 1957 see claims 4,8 ---	21,22, 24,25
A	FR,A,1 416 295 (ARMOUR ET COMP.) 20 September 1965 see example 9 ---	23
X	US,A,5 084 197 (GALIC ET AL.) 28 January 1992 see column 9, line 34 - line 45 see column 24, line 31 - line 42 ---	26
A	US,A,3 313 736 (DICKSON ET AL.) 11 April 1967 see the whole document -----	1-27



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(information on patent family members)

Int. .onal Application No

PCT/EP 93/02560

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		US-A- 3265512	
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